

## IV.A.5p Neutron Characterization and Calphad in Support of the Metal Hydride Center of Excellence

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### Introduction

In search of a hydrogen-storage material that meets the DOE technical targets, the Metal Hydride Center of Excellence (MHCoE) has been investigating the possibilities of destabilizing the light-metal alkali and alkaline-earth hydrides by doping with Group IV A elements. Using neutron-based probes, the NIST has provided diffraction and spectroscopic characterization of LiH, NaH, CaH<sub>2</sub>, and MgH<sub>2</sub> compounds and/or co-mixtures destabilized with Si or Ge. These combinations are being studied to help understand the effect of doping on the structure and hydrogen bonding associated with these light-metal alloy systems, since doping ultimately influences hydride stabilities and hydrogen-cycling properties. In addition, we have begun neutron characterization of light-metal borohydride systems such as LiBH<sub>4</sub> and Ca(BH<sub>4</sub>)<sub>2</sub> and have investigated the hydrogen-cycling properties of LiBH<sub>4</sub> mixed with either ScH<sub>2</sub> or CaH<sub>2</sub>.

Calphad thermodynamic modeling provides critical assessments of hydrogen content, character and heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoE-developed metal-hydride systems. NIST has expanded the existing Li-Mg-B-Si-H thermodynamic database by adding the ternary compound LiBH<sub>4</sub> and the element Ca and its respective binary phases. A provisional thermodynamic description has been developed for the Li-B system. The expanded database has been used to calculate the reactions in quaternary hydrogen systems. These results are the basis for the evaluation of the suitability

of destabilization reactions from adding binary hydrides MgH<sub>2</sub> and CaH<sub>2</sub> to LiBH<sub>4</sub>.

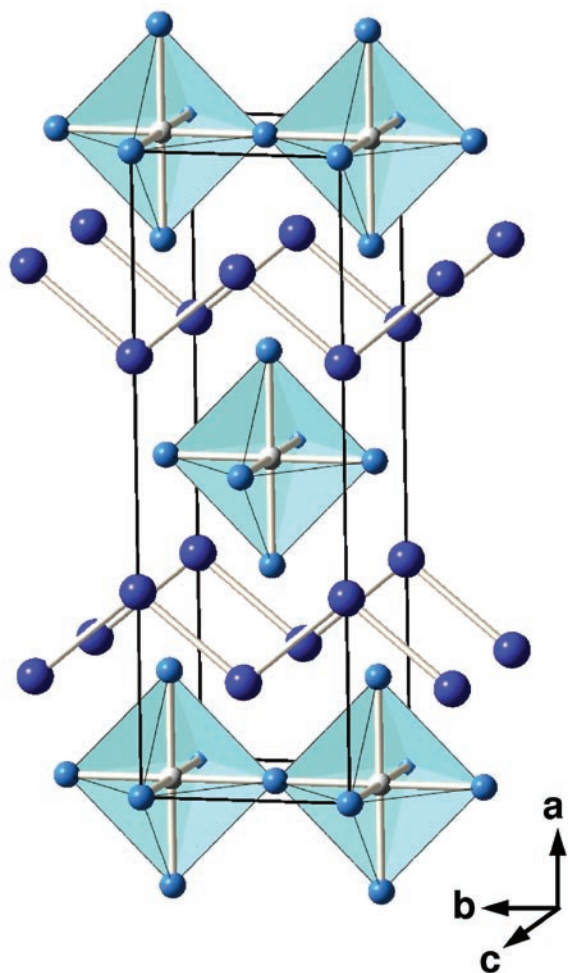
### Approach

The key to improved hydrogen-storage materials is a detailed understanding of the atomic-scale locations and lattice interactions of the hydrogen. We are applying our state-of-the-art neutron measurement capabilities and expertise at the NIST Center for Neutron Research (NCNR) to the promising materials being developed by the MHCoE. This work enables MHCoE partners to obtain unique insights into the atomic- and molecular-scale properties that are responsible for the hydrogen-storage properties of these candidate materials.

In addition, we are performing Calphad thermodynamic modeling. The available literature has been evaluated for thermodynamic data and analytical descriptions of the thermodynamic functions of the relevant phases. The data and functions are compiled into a consistent database describing the multi-component systems. Missing quantities are identified and descriptions are being developed in collaboration with MHCoE partners.

### Results

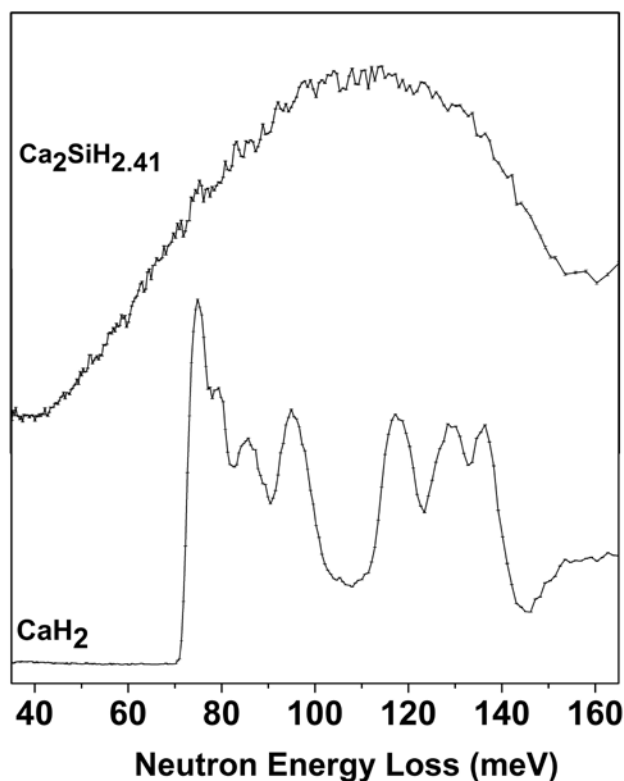
We have focused the majority of our neutron measurements on destabilized light-metal hydrides in order to gain a more fundamental understanding of the role of the destabilizer element. In collaboration with the Jet Propulsion Laboratory (JPL), Hughes Research Laboratory (HRL), and Caltech, we were finally able to determine, by neutron powder diffraction (NPD) and neutron vibrational spectroscopy (NVS), the structure and hydrogen bonding associated with the newly discovered Li-Si-H and Li-Ge-H ternary phases mentioned in last year's annual report. The novel Li<sub>4</sub>Si<sub>2</sub>H and Li<sub>4</sub>Ge<sub>2</sub>H phases have an isomorphic orthorhombic *Cmmm* structure (Figure 1) [1], with all H atoms located in identical Li<sub>6</sub>-defined octahedra. These corner-shared octahedra are situated in two-dimensional sheets in the *bc* plane and stacked in the *a* direction between sheets of zigzagging Si or Ge chains. Li-H bond distances are similar to those in LiH. First-principles calculations corroborate the observed structure and associated vibrational modes and confirm that strong Li-H binding is primarily responsible for the stability of these unique ternary phases. Unfortunately, this stability hinders the desired complete hydrogenation of Li atoms to LiH during normal hydrogen cycling of these doped systems.



**FIGURE 1.** An Off-[001] view of the orthorhombic structure of the new ternary hydrides  $\text{Li}_4\text{Si}_2\text{H}$  and  $\text{Li}_4\text{Ge}_2\text{H}$ . The large dark and small light spheres represent Si (or Ge) and Li, respectively, and the interstitial H atoms are centered in the shaded  $\text{Li}_6$  octahedra.

We have continued our investigations of Ca-Si alloy systems, specifically crystalline  $\text{Ca}_2\text{Si}$  formed by evacuative  $\text{H}_2$  desorption of  $2\text{CaH}_2 + \text{Si}$  mixtures [2].  $\text{Ca}_2\text{Si}$  absorbs hydrogen much more readily than  $\text{CaSi}$ , with fairly rapid uptake (i.e., the majority occurring in minutes) at 473–573 K for  $\text{H}_2$  pressures even  $<1$  atm. At higher  $\text{H}_2$  pressures  $>5$  atm, NPD, NVS, and isotherm measurements indicate that  $\text{Ca}_2\text{Si}$  surprisingly forms an amorphous hydride  $\text{Ca}_2\text{SiH}_{2.41}$  (Figure 2) that can be cycled back to the crystalline  $\text{Ca}_2\text{Si}$  phase upon dehydrogenation. This is the first observation of hydrogen-induced amorphization in a C37 alloy and suggests a possible pathway for developing new hydride materials with improved absorption kinetics.

With this discovery, we further pursued the alloying of  $\text{Ca}_2\text{Si}$  with  $\text{Mg}_2\text{Si}$  in an attempt to make  $\text{Mg}_2\text{Si}$  more hydridable. Evacuative dehydrogenation of various ball-milled  $(2-x)\text{CaH}_2 + x\text{MgH}_2 + \text{Si}$  mixtures ( $0 \leq x \leq 1$ ) indicated that a single  $\text{Ca}_2\text{Si}$ -like phase exists only for



**FIGURE 2.** Spectrum of Amorphous  $\text{Ca}_2\text{SiH}_{2.41}$  Compared to That of Crystalline  $\text{CaH}_2$

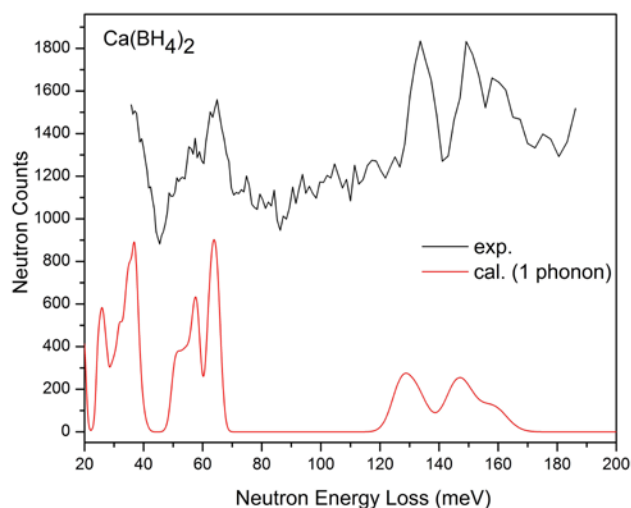
$x=1$ , forming  $\text{CaMgSi}$ . All other compositions form the two-phase mixture  $(1-x)\text{Ca}_2\text{Si} + x\text{CaMgSi}$ . It was determined by NPD, NVS, and isotherm measurements that  $\text{CaMgSi}$  hardly absorbs  $\text{H}_2$  even at 70 atm and 473–573 K. Moreover, hydrogenation of the various  $(1-x)\text{Ca}_2\text{Si} + x\text{CaMgSi}$  mixtures was found to be dominated by the fraction of  $\text{Ca}_2\text{Si}$  present, with the  $\text{CaMgSi}$  fraction remaining relatively inert [3]. Therefore, the substitution of Mg for Ca in the  $\text{Ca}_2\text{Si}$  structure failed to render the Mg more reactive to hydrogen.

We undertook NPD and NVS characterization of the Na-Mg-Si-H quaternary system. Again, although  $\text{Mg}_2\text{Si}$  is very hard to hydride,  $\text{NaSi}$  is more capable of reversibly absorbing  $\text{H}_2$ . We first determined that the dehydrogenation/hydrogenation of a  $\text{NaH}+\text{MgH}_2$  ball-milled mixture forms the  $\text{NaMgH}_3$  phase at 623 K and 50 atm. This ternary phase underwent dehydrogenation to Na and Mg at 623 K. With this knowledge, we next evacuated a  $\text{NaH} + 2\text{MgH}_2 + 2\text{Si}$  ball-milled mixture at 623 K to form  $\text{Mg}_2\text{Si} + \text{NaSi}$ . Rehydrogenating this alloy mixture at 623 K and 50 atm led to the products  $(1-x)\text{Mg}_2\text{Si} + (1-x)\text{NaH} + \text{Si} + x\text{NaMgH}_3$ . In other words, we found that the addition of Na to  $\text{Mg}_2\text{Si}$  enabled its partial hydrogenation through the formation of  $\text{NaMgH}_3$ .

We have provided both structural and dynamical characterization of the low-temperature and high-temperature phases of  $\text{LiBH}_4$  by synthesizing isotopically labeled  $^7\text{Li}^{11}\text{BH}_4$  and  $^7\text{Li}^{11}\text{BD}_4$  followed by NPD and NVS measurements [4]. This allowed us to avoid the considerable neutron absorption problems associated with  $^6\text{Li}$  and  $^{10}\text{B}$  atoms. The B–H bond lengths and H–B–H angles for the  $\text{BH}_4^-$  tetrahedra indicated that the tetrahedra maintained a nearly ideal configuration throughout the temperature range investigated. The atomic displacement parameters at 360 K suggest that the  $\text{BH}_4^-$  tetrahedra become increasingly disordered as a result of large-amplitude librational and reorientational motions as the orthorhombic to hexagonal phase transition temperature (384 K) is approached. In the high-temperature hexagonal phase, the  $\text{BH}_4^-$  tetrahedra displayed extreme disorder about the trigonal axis along which they are aligned. NVS data were in agreement with prior Raman spectroscopy and low-resolution NVS studies.

As another example of characterization of samples from other partners, we have investigated a  $\text{Ca}(\text{BH}_4)_2$  sample provided by Sandia National Laboratory (SNL). SNL synthesized the  $\text{Ca}(\text{BH}_4)_2$  from the high-pressure hydrogenation of  $2\text{CaH}_2 + \text{CaB}_6$ . Our NVS measurement (Figure 3) provided spectroscopic verification of  $\text{Ca}(\text{BH}_4)_2$  based on agreement with first-principles phonon calculations of the published  $\text{Ca}(\text{BH}_4)_2$  structure [5].

We also investigated two systems suggested by MHCoe theorists as possible hydrogen-storage candidates [6]: (1)  $2\text{LiBH}_4 + \text{ScH}_2 \rightarrow \text{ScB}_2 + 2\text{LiH} + 4\text{H}_2\uparrow$  (8.9 wt%), and (2)  $6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2\uparrow$  (11.7 wt%). For the former, dehydrogenation



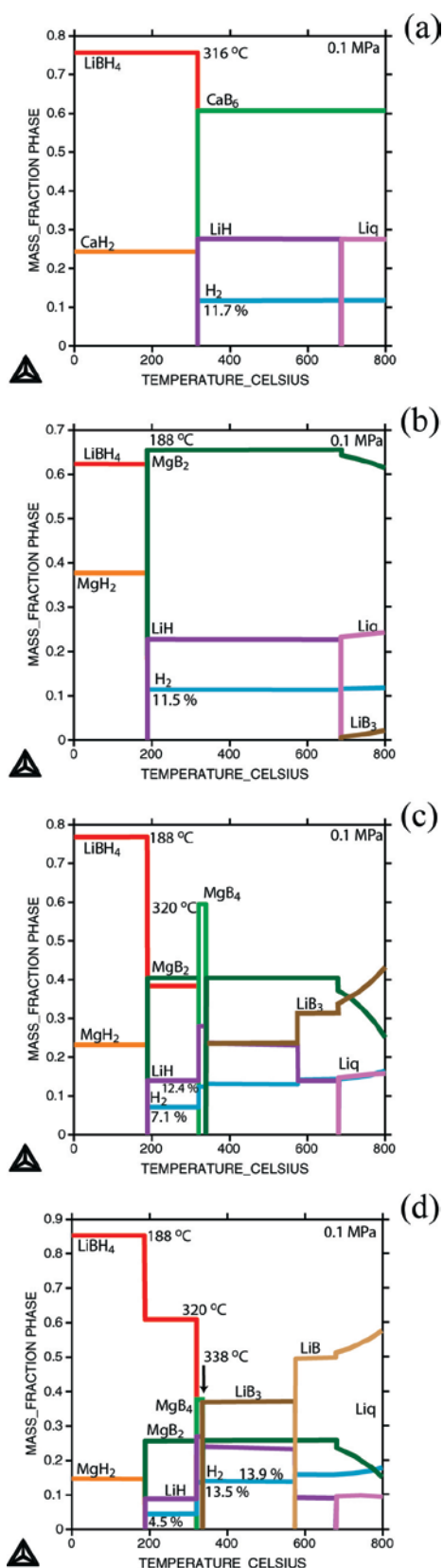
**FIGURE 3.** NV Spectrum of a High-Pressure-Synthesized  $\text{Ca}(\text{BH}_4)_2$  Sample from Sandia (upper black line) Compared to That Computed from First Principles (lower red line)

occurred above 653 K (in ~6 hours) and no appreciable  $\text{H}_2$  absorption occurred during the rehydrogenation step. For the latter, dehydrogenation occurred above 653 K (in ~2-3 hours) and rehydrogenation was achieved at 653 K and 50 atm (in ~1 day). Subsequent results from other partners suggested that the dehydrogenation of these borates leads to elemental boron, not borides, so that the suggested reaction sequences above may be inaccurate.

The thermodynamic Calphad database including the elements Li, Mg, B, H and Si has been expanded by the addition of the ternary compound  $\text{LiBH}_4$  and the addition of Ca and the respective binary phases. The database was used to calculate the reaction paths of different hydride mixtures, *viz.*,  $6\text{LiBH}_4 + \text{CaH}_2$  and  $n\text{LiBH}_4 + \text{MgH}_2$  ( $n = 2, 4, 7$ ). In all four cases, the calculations show that a destabilization of the hydrides occurs and the reaction temperature is lowered. The calculations also showed that for the different  $n\text{LiBH}_4 + \text{MgH}_2$  mixtures, hydrogen is released in one reaction step only for  $n = 2$ , while for  $n = 4$  and 7, multiple reaction steps occur. However, due to the lack of data for the binary Li-B system, the original version of the database did not include a description and, therefore, did not allow evaluation whether formation of binary Li-B compounds would alter the calculated reaction paths. A provisional thermodynamic description of this system was developed using first-principles data from the MHCoe partners at Carnegie Mellon University and the University of Pittsburgh. This description has been included in the database. The reaction path calculations were repeated and showed that no formation of Li-B compounds occurred for the  $6\text{LiBH}_4 + \text{CaH}_2$  mixture. For the  $n\text{LiBH}_4 + \text{MgH}_2$  mixtures, Li-B compounds formed at higher temperatures, but their formation did not affect the hydrogen release reactions at lower temperatures. The reaction paths of the four mixtures are shown in Figure 4. The calculations show that the mixture  $2\text{LiBH}_4 + \text{MgH}_2$  is the most promising of these mixtures for hydrogen storage because 11.5% hydrogen is released in one reaction at a fairly low temperature of 188°C.

## Conclusions and Future Directions

- Neutron methods and Calphad computations provided crucial, non-destructive characterization and predictive tools for the MHCoe. NIST collaborated with at least seven partners in FY 2007.
- Combined neutron and first-principles studies reveal novel ternary structures and H bonding for hydrided Li and Ca alloyed with Si (Ge). Nonetheless, the formation of these structures decreases the maximum H uptake expected for these destabilized materials. Also the H desorption temperature is still too high for practical applications.



**FIGURE 4.** Reaction Paths for Mixtures of  $\text{LiBH}_4$  with Binary Metal Hydrides, (a)  $6\text{LiBH}_4 + \text{CaH}_2$ , (b)  $2\text{LiBH}_4 + \text{MgH}_2$ , (c)  $4\text{LiBH}_4 + \text{MgH}_2$ , (d)  $7\text{LiBH}_4 + \text{MgH}_2$

- Hydrogen-induced amorphization (HIA) observed for  $\text{Ca}_2\text{Si}$  suggests a possible pathway for developing new hydride materials with improved absorption kinetics and warrants further examination.
- Attempts to render  $\text{Mg}_2\text{Si}$  more hydridable by alloying with  $\text{Ca}_2\text{Si}$  or  $\text{NaSi}$  were only partially successful. Although the  $\text{CaMgSi}$  alloy that routinely formed using  $\text{Ca}_2\text{Si}$  could not be hydrided under normal conditions, some of the  $\text{Mg}_2\text{Si}$  hydrided when  $\text{NaSi}$  was present to form  $\text{NaMgH}_3$ . This suggests that proper doping of  $\text{Mg}_2\text{Si}$  with additional elements can render the Mg component more reactive.
- Neutron methods confirm the formation of  $\text{Ca}(\text{BH}_4)_2$  from the high-pressure hydrogenation of  $2\text{CaH}_2 + \text{CaB}_6$ . These high-pressure syntheses using borides may provide an alternate means of incorporating neutron-transparent  $^{11}\text{B}$  into various borohydrides to enable better neutron measurements.
- Hydrogen cycling measurements of promising destabilizing combinations of  $\text{LiBH}_4$  with  $\text{ScH}_2$  and  $\text{CaH}_2$  indicate that they may be hindered by the formation of elemental boron during dehydrogenation.
- The Calphad phase equilibria calculations of reaction paths for four hydride mixtures,  $6\text{LiBH}_4 + \text{CaH}_2$  and  $n\text{LiBH}_4 + \text{MgH}_2$  ( $n = 2, 4, 7$ ), show that  $2\text{LiBH}_4 + \text{MgH}_2$  is the most promising of these mixtures for hydrogen storage because 11.5% hydrogen is released in a one-step reaction at a fairly low temperature of  $188^\circ\text{C}$ .
- We will continue to provide neutron metrology and Calphad computations to other MHCoE partners on hydrogen-storage materials of interest.
- We will continue to explore potentially promising ternary and quaternary light-metal-based systems.
- We will continue to probe structures and H dynamics for  $\text{BH}_4$ -related systems, possibly using  $^{11}\text{B}$ , in conjunction with MHCoE partners, including studies of borohydrides in nanoporous media to improve  $\text{H}_2$ -release characteristics.
- We will collaborate with Stanford University on using neutron reflectometry to characterize hydrogenation/dehydrogenation processes associated with light-metal thin films.
- We will develop a second thermodynamic database for multi-component Na-K-B-H. This database will be compatible with the existing six-component database.

### Special Recognitions

1. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, "Investigation of Novel Systems for Hydrogen Storage: Synthesis, Neutron Scattering and First-principles



Calculations,” named Outstanding Poster Presentation in Materials category at the 14th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD (February, 2007).

2. T. J. Udovic co-chaired the International Symposium on Metal-Hydrogen Systems, Lahaina, HI (October, 2006).

## FY 2007 Publications/Presentations

1. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, and T. Yildirim, “Structure and Hydrogen Bonding in  $\text{CaSiD}_{1+x}$ : Issues about Covalent Bonding,” *Phys. Rev. B* **74**, 224101 (2006).
2. H. Wu, M. R. Hartman, T. J. Udovic, J. J. Rush, W. Zhou, R. C. Bowman, Jr., and J. J. Vajo, “Crystal Structure of a Novel Class of Ternary Hydrides  $\text{Li}_4\text{Tl}_2\text{D}$  ( $\text{Tl}=\text{Si}$  and  $\text{Ge}$ ),” *Acta Cryst. B* **63**, 63 (2007).
3. H. Wu, W. Zhou, T. J. Udovic, and J. J. Rush, “Hydrogen Storage in a Novel Destabilized Hydride System,  $\text{Ca}_2\text{SiH}_x$ : Effects of Amorphization,” *Chem. Mat.* **19**, 329 (2007).
4. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, “Structure and Vibrational Spectra of Calcium Hydride and Deuteride,” *J. Alloys Compd.* **436**, 51 (2007).
5. M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman, Jr., and S.-J. Hwang, “Structure and Vibrational Dynamics of Isotopically Labeled Lithium Borohydride Using Neutron Diffraction and Spectroscopy,” *J. Solid State Chem.* **180**, 1298 (2007).
6. H. Wu, W. Zhou, and T. Yildirim, “Hydrogen Storage in a Prototypical Zeolitic Imidazolate Framework-8,” *J. Am. Chem. Soc.* **129**, 5314 (2007).
7. H. Wu, W. Zhou, T. J. Udovic, and J. J. Rush, “Structure and Hydrogenation Properties of the Ternary Alloys  $\text{Ca}_{2-x}\text{Mg}_x\text{Si}$  ( $0 \leq x \leq 1$ ),” *J. Alloys Compd.* (2007), doi:10.1016/j.jallcom.2007.01.018.
8. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, M. R. Hartman, R. C. Bowman, Jr., and J. J. Vajo, “Neutron Vibrational Spectroscopy and First-Principles Study of Novel Ternary Hydrides:  $\text{Li}_4\text{Si}_2\text{H(D)}$  and  $\text{Li}_4\text{Ge}_2\text{H(D)}$ ,” *Phys. Rev. B* (submitted May 2007).
9. U. R. Kattner, “A Thermodynamic Database for Metal Hydrogen Systems,” MH2006 International Symposium on Metal Hydrogen Systems, Lahaina, HI (October, 2006).
10. M. R. Hartman, J. J. Rush, T. J. Udovic, T. Yildirim, “Quasielastic Neutron Scattering Investigation of the Reorientational Motion of Hydrogen in  $\text{Na}_3\text{AlH}_6$  and  $^7\text{Li}^{11}\text{BH}_4$ ,” MH2006 International Symposium on Metal Hydrogen Systems, Lahaina, HI (October, 2006). (Invited).
11. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, and T. Yildirim, “Neutron Scattering Study of the Structure, Phase Variation, and Properties of Si-Destabilized Calcium Hydrides,” MH2006 International Symposium on Metal Hydrogen Systems, Lahaina, HI (October, 2006).
12. H. Wu, M. R. Hartman, T. J. Udovic, J. J. Rush, W. Zhou, R. C. Bowman, Jr., J. J. Vajo, “Crystal Structure of a Novel Class of Ternary Hydrides  $\text{Li}_4\text{Tl}_2\text{D}$  ( $\text{Tl}=\text{Si}$  and  $\text{Ge}$ ),” MH2006 International Symposium on Metal Hydrogen Systems, Lahaina, HI (October, 2006).
13. R. C. Bowman, Jr., S.-J. Hwang, C. C. Ahn, J. J. Vajo, M. R. Hartman, T. J. Udovic, J. J. Rush, “Destabilization Behavior and Phase Compositions for  $\text{LiH-Ge}$ ,” MH2006 International Symposium on Metal Hydrogen Systems, Lahaina, HI (October, 2006).
14. T. J. Udovic, “Probing Structure and Bonding in Hydrogen-Storage Materials by Combined Neutron-Scattering Techniques and First-Principles Calculations,” Department of Physics, Washington University, St. Louis, MO (October, 2006). (Invited).
15. H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, “Investigation of Novel Systems for Hydrogen Storage: Synthesis, Neutron Scattering and First-principles Calculations,” 14th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD (February, 2007).
16. H. Wu, “Structure and Bonding in Destabilized Metal Hydrides for Hydrogen Storage,” American Physical Society Meeting, Denver, CO (March, 2007). (Invited).
17. W. Zhou, H. Wu, T. Yildirim, “Structure, Lattice Dynamics, and Hydrogen Adsorption Properties of Zeolitic Imidazolate Framework-8,” American Physical Society Meeting, Denver, CO (March, 2007).
18. J. J. Rush, W. Zhou, H. Wu, T. J. Udovic, T. Yildirim, “Quantum Methyl Rotations in Zeolitic Imidazolate Framework-8: Inelastic Neutron Scattering and First-principles Calculations,” American Physical Society Meeting, Denver, CO (March, 2007).
19. T. J. Udovic, H. Wu, W. Zhou, J. J. Rush, T. Yildirim, “Hydrogen Bonding in  $\text{CaSiH(D)}_{1+x}$ : Is there Covalent Character?” American Physical Society Meeting, Denver, CO (March, 2007).
20. U.R. Kattner, “Thermodynamic Calculations of Metal-Hydrogen Systems,” Symposium on Phase Stability and Defect Structures in Advanced Materials to Honor Austin Chang, Orlando, FL (March, 2007). (Invited).
21. U.R. Kattner, S.V. Alapati, J.K. Johnson, and D.S. Sholl, “Challenges in the Development of a Thermodynamic Database for Metal-Hydrogen Systems,” CALPHAD XXXVI, State College, PA (May, 2007).

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4. M. R. Hartman *et al.*, *J. Solid State Chem.* **180**, 1298 (2007).
5. K. Miwa *et al.*, *Phys. Rev. B* **74**, 155122 (2006).
6. S. P. Alapati *et al.*, *Phys. Chem. Chem. Phys.* **9**, 1438 (2007).